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SELECTIVE SORBENTS FOR ONTARIO HYDRO NUCLEAR SYSTEMS - A PRELIMINARY APPRAISAL

Report No. 87-216-K

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ABSTRACT

A review of the relevant literature and current technologies for removal of radioactive isotopes of long life spans from CANDU purification systems has been carried out as part of Ontario Hydro's programme to evaluate selective sorbents to reduce the costs involved in ion exchange media replacement and disposal. Initial screening tests have identified two Union Carbide zeolites A-51 and X-61; and organic chelating resins ES 467 and IRC 718 from Rohm and Haas Company, as being worthy of further investigation for cobalt removal. Additionally, several proprietary sorbents specifically designed for nuclear waste removal will be evaluated.

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EXECUTIVE SUMMARY

SELECTIVE SORBENTS FOR ONTARIO HYDRO NUCLEAR SYSTEMS - A PRELIMINARY APPRAISAL

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The conventional organic ion exchange resins currently in use in the nuclear purification circuits at various Ontario Hydro's CANDU stations lack sufficient selectivity for long-lived nuclear species, and consequently they are under-used and continue to generate large volumes of nuclear waste adding to the cost of handling.

A programme has been initiated with the objective of identifying and developing suitable sorbent materials with high selectivities for specific chemical species of interest (eg: Cs/Sr in PHT and Co in moderator) to minimize IX replacement and waste resin storage costs.

An extensive literature survey has identified a variety of materials such as porous glass based sorbents, other sorbents with immobilized chemical functional groups and synthetic and natural inorganic ion-exchangers as possible replacements for the conventional organic ion exchangers presently in use. Additionally, some novel sorbents may be synthesized.

The initial phase of the test programme is concerned with the testing of readily available commercial sorbents and some results of preliminary examinations have been reported. The next phase will involve the testing of some proprietary sorbents, commercially available non-proprietary inorganic and a few organic sorbents. It is also hoped to synthesize and test a few inorganic ion-exchangers and a few organic exchangers of high specificity for species of interest. In all cases, the test results will be compared directly with those of the resins presently in use at the stations.

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Preliminary bench scale static tests, so far, have identified two Union Carbide zeolites A-51 and X-61 and organic chelating resins ES467 and IRC 718 from Rohm and Haas Company as being worthy of further investigation for cobalt removal.

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To Mr. H.N. Isaac
Manager
Nuclear Materials Management
Design and Development Division - Generation

Attention: Mr. R.E. Heathcock

SELECTIVE SORBENTS FOR ONTARIO HYDRO NUCLEAR SYSTEMS - A PRELIMINARY APPRAISAL

1. INTRODUCTION

The importance of water chemistry of the aqueous systems associated with the CANDU-PHW reactors in reducing radiation exposure at and extending the plant life of nuclear powered electricity generating systems cannot be overemphasized (1a).

In Ontario Hydro organic ion exchange resins have been used as the chief means of purifying the various nuclear aqueous circuits (Table I). These organic ion exchangers not only perform the function of removing soluble corrosion and fission reaction products, but also help to keep some of the chemistry control parameters such as pH within specifications.

Although these organic ion exchangers have operated satisfactorily over the years they suffer from lack of selectivity towards metal ions in solution. Further, the extremely low concentration of the dissolved species limit the exploitation of the full potential capacities of the exchangers (1b).

While the nature and the quantity of chemical species present is a function of the given circuit (2), the location of the circuit, the operational history etc., the chief species responsible for relatively long-lasting radioactivity include radiocaesium and cobalt.

Recognizing the substantial potential for reductions in replacement cost and waste storage costs, Ontario Hydro has embarked on a programme to identify and develop alternate sorbents with high selectivity towards long-lived radioactive species. This report atttempts to examine the suitability and applicability of various sorbents of potential selectivity towards species of interest.

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2. OBJECTIVE

The objective of the programme is to (a) identify and develop arrangements and/or sorbents with significant selectivities towards cobalt and caesium, to replace or augment the existing organic ion exchange systems and (b) demonstrate through field testing the effectiveness of the identified alternatives.

3. SCOPE

While the search could be very broad in scope, primary focus will be on alternatives which may be used with little or no modifications to the existing hardware at the stations. Selection of nonproprietary, commercially available ion exchange media in good supply and at reasonable costs will be preferred. The testing will include (a) selection and/or synthesis of ion exchange media (b) bench scale testing (c) pilot testing and (d) process evaluation.

The ideal initial approach in the laboratory testing would be to simulate the actual operating conditions prevailing in the different purification systems of the nuclear generating stations. However, this is likely to be somewhat difficult due to lack of sufficient analytical data on the chemical composition of the various aqueous circuits.

The few reports (3-5) of analysis of spent ion-exchange resins from PHT and moderator systems and the reports (5b) on activity transport studies are, perhaps, the only sources of information available so far to indicate the possible chemical composition of Ontario Hydro's CANDU systems. The ionic composition of two actual heavy water samples taken after a brief period of operation of Hydro-Québec's Gentilly 2 moderator system has been reported (6). The ^{60}Co concentration for the same system has been observed (7) to lie within the range of 0.6 - 19 μCi/kg of D_2O whilst the corresponding value for the PHT system has generally been below 0.1 μCi/kg of D_2O. These limited studies, however, have established that ^{60}Co is the major gamma emitter in the moderator resin and that radio caesium is the major contributor to the gamma field of the primary heat transport resin.

In the course of the present study, it is hoped to obtain more sample data on these systems. In the meantime, a pragmatic approach would be to try and estimate the qualitative composition of various aqueous circuits based on the possible corrosion products from materials of construction and possible products

from nuclear fission reactions and combine these with Hydro-Québec's data. The impact of uncertainties in the possible chemical composition of the feed water solution will be minimized by the proposed small column (~100 mL) testing at the stations in a loop of an existing purification circuit.

4. REVIEW OF SOME PURIFICATION METHODS AND SORBENTS AVAILABLE

Many nuclear facilities, including R and D establishments which produce site effluents containing a wide range of radionuclides often in variable quantities, have used a variety of treatment methods for such wastes.

In general, some form of chemical precipitation has been preferred for the clean up of such wastes, but ion exchange may then be used to "polish" the effluent by removing one or more particular radionuclides which are insufficiently removed by the main treatment. Several examples of this use of ion exchangers for polishing a treated waste are available in the United States (8) where natural or artificial zeolites are used at a number of plants to remove particularly caesium. Another such application is at the French reprocessing plant of Cap la Hague where nickel ferrocyanide precipitation is used to remove alpha activity and caesium, followed by passage of the stream through a carboxylic exchanger in the sodium form for the removal of strontium (9). The same source mentions of a Russian application using ferric hydroxide precipitation followed by cation and anion columns to treat waste from research institutes; use of bone char and active carbon to remove actinides, and the use of preformed ferrites as an alternative to in-situ precipitation of the same materials.

Precipitation processes have also been considered for removal of caesium. For example, precipitation processes using either sodium tetraphenyloborate (NaTPB) or phosphotungstic acid (PTA) as precipitating chemicals have been evaluated (10) amongst other methods to remove caesium from alkaline PUREX supernatant solutions. NaTPB has high decontamination factors ($DF>10^5$) for caesium; however, a large-scale demonstration at Savannah River Laboratory has revealed that substantial radiolytic decay of the NaTPB occured releasing detectable quantities of benzene vapour. The PTA precipitation process requires repeat precipitation of the supernatant solution to achieve high overall decontamination factors. Despite this disadvantage, however, the resultant precipitate can be incorporated directly into a glass product.

Both precipitation processes mentioned above suffer from extensive equipment and process complexity.

Of the many methods available for separation, column extraction techniques offer relatively high concentration factors and the ability of treating large volumes in a closed system free from contamination. These column techniques may involve the use of columns packed with ligand-immobilized or ligand-impregnated materials or conventional sorbents requiring pretreatment of the metal solution with a complexing agent.

The various sorbents that are available and of interest may be broadly classified into the following categories:

4.1 Organic Ion Exchange Resins. The cationic component of the mixed resins presently in use in Ontario Hydro's CANDU systems being ofstrong catonic type is not expected to show significant selectivities towards metal ions. However, some phenol-formaldehyde polymers are known to exhibit high selectivities. For example, Duolite ARC-359 is said to have a high selectivity for ^{137}Cs in alkaline media and is believed to be resistant to radiation damage. Others include Bayer Lewatit® DNKR (Research Division personnel have investigated this before) and Duolite CS-100 which are claimed by the manufacturers to be good for caesium removal in the pH range 6-14.

4.2 Chelating Ion Exchange Resins. The use of coordinating copolymers to extract various radionuclides from nuclear wastes is the subject of several investigations (11). Among the ones investigated for ^{106}Ru removal from pond waters are a dithiocarbamate copolymer (K_D=13,800), a thiadiazole copolymer (K_D= 1,550), a thiol copolymer (K_D=800) and amidinothiourea (K_D= 24,600) which were all found to be stable to radiolytic decay after extracting ^{106}Ru from 3.6×10^{-6} molar solutions for periods up to four weeks. It is suggested that copolymers which are cross-linked with divinylbenzene are too inflexible to allow some metals to have six-fold coordination but thiols may not have this problem.

Coordinating copolymers are versatile reagents which can be made selective for particular types of metals such as actinide separation from lanthanides, precious metals from base metals or precious metals from actinides. However, they are suceptible to radiolytic damage and display slower rates of reaction.

Table 3 summarizes the various types of chelating resins that are commercially available. All of them are expected to be very selective towards transition metals and other divalent metals

such as alkaline earth metals. For cobalt removal, several chelating resins are available and some of them may be good for strontium removal as well:

eg Bayer Lewatit OC 1014 containing sulphur and nitrogen chelate group.

Amberlite IRC 718 with iminodiacetic acid group
Duolite SE 467 with aminophosphonic acid group
Duolite ES 346 with amidoxime group
Duolite GT 73

4.3 Inorganic Ion Exchangers. A considerable volume of information is available on the use of inorganic ion exchangers for nuclear waste stream decontamination (12).

In general, inorganic ion exchangers possess many superior properties which make them more suitable than organic exchange resins for the treatment of radioactive waste solutions. Unlike organic resins, the functional group is an integral part of the material and as such both structure and exchange properties are governed by the same chemical composition. Further, inorganic exchangers are believed to be more compatible than organic resins with hydrated cement-based matrices used for waste immobilization.

The materials of interest include natural inorganic exchangers (clay minerals and zeolites), synthetic zeolites, oxides and hydrous oxides, acidic salts of multivalent metals and cyanoferrates which have all found applications in the treatment of nuclear waste solutions. Natural inorganic materials are limited, amongst other things, by their relatively low ion exchange capacities and their tendency to peptize, ie, to form colloids in some solutions. Synthetic zeolites are commerically available and act as molecular sieves by excluding ions larger than the opening in the cyrstalline matrix. They possess improved stability and higher exchange capacity. Many of these compounds exhibit unusual selectivity towards metal ions and also they seem to be little affected by high radiation.

With zeolites, ion exchange is controlled by diffusion within the solid, and the diffusion rate constants are some 10^6 times lower than those for organic resins. Also, because of soluble Al and Si content, specially at elevated temperatures the usefulness of zeolite exchangers in hot water purification is very limited.

Some commercial zeolites of interest include Union Carbide's A-51, X-61 for cobalt selectivity, IE-96 for caesium selectivity and mordenites of various descriptions from the PQ corporation. In a recent investigation to determine the technical and

economic feasibility of an alternative treament process, a combination of a zeolite (large port mordenite) and organic exchange media has been successfully used (13) to treat aerated waste liquid at the Millstone Nuclear Station. This system achieved decontamination factors (DF) in excess of 1000 for ^{137}Cs, 300 for ^{60}Co, 150 for ^{131}I after 5700 column volumes of waste had been treated. The activated carbon used in a leading column did not contribute significantly to the volume reduction but increased the transportation and burial costs. A cost analysis had revealed 60-75% reduction in the cost of ion exchange media replacement and disposal using the proposed ion exchange system at this plant.

Only a few of the oxide and hydroxide materials are available in commercial quantities. Many show high exchange capacity, low solubility and good radiation and thermal stability. They are generally amphoteric favouring anion exchange at low pH and cation exchange at high pH. They are most active when freshly precipitated and are generally regarded as least useful for column applications. On the other hand acidic salts of multivalent metals and cyanoferrates offer more potential applications although they too are not available in commercial quantities and many are likely to be expensive to produce.

A large number of acid salts of group IV B metals (Ti, Zr, etc in the oxidation state IV) with acids of group V A elements (P, As, Sb, Bi) have been characterized and found to possess ion exchange properties (14). For example, addition of a soluble Zr(IV) salt to phosphoric acid results in the precipitation of an amorphous solid which on refluxing changes to a stoichiometric crystalline compound $Zr(HPO_4)_2 \cdot H_2O$ which readily exchanges sodium ions. The observed selectivity at pH 2 for zirconium phosphate (γ-ZrP) exchangers is $K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$.

Although both amorphous and crystalline forms of inorganic exchangers such as zirconium phosphate exhibit interesting ion exchange behaviour, they have not been fully explored due to several reasons.

(a) the solids do not lend themselves to conventional column use.
(b) they exhibit poor hydrodynamic properties.
(c) they tend to bleed phosphate in alkaline solutions
(d) they are difficult to produce with consistent quality.
(e) the ion exchange behaviour seems to be a function of the crystallizing and structure.

Several recent developments have largely taken care of these deficiencies.

The French Atomic Energy Commission utilizes a mixed bed exchanger consisting of zirconium phosphate and ammonium phosphotungstate in a process called ELAN. A large degree of separation of radioisotpes has been reported. There are claims of complete separation of ^{137}Cs from other fission products.

Materials which show most promise for high temperature water purification are hydrous zirconium oxide and zirconium phosphate. Materials containing Si or Al are in general, not satisfactory because of the release of these ions. Some examples of interest are:

(i) Tin (IV) Antimonate for Cs (Ref 15)

(ii) Zn_2 $[Fe(CN)_6] \cdot xH_2O$ has excellent adsorption power for Cs (Ref 16)

(iii) NH_4 Mg PO_4 $6H_2O$ has been found to have good separation coefficients for Cs^+ - Rb^+ etc. (Ref 17)

The reversibility of NH_4^+ - M^+ (M=Cs, Rb, or K) exchange on the phosphate is good.

(iv) Stannic tungstophosphate for bivalent ions such as Co^{2+} (Ret 18)

(v) Lithium niobate crystals, $LiNbO_3$ show interesting reversible mechanism involving lithium in the crystals (may be used for Co^{2+}, or Fe^{2+} etc) (Ref 19)

(vi) Chromium ferricyanide gel (CFiC): The stability of this gel in both acidic and salt solutions and its high specificity for caesium are said (20) to be responsible for its good scavenger properties in removing long-lived ^{137}Cs from radioactive waste. Also it is mentioned that cobalt ferrocyanide is superior by a number of workers in that Cs^+ is irreversibly adsorbed on it along with Co, Zn, La.

(vii) Copper ferrocyanide: It is known that copper ferrocyanide has a high affinity for caesium and can preferentially co-precipitate it in the presence of relatively high amounts of other alkali or alkaline earth cations. A recent report (21) claims over 99% removal of caesium using sodium lauryl sulphate, cetyl trimethyl ammonium

bromide or gelatin as collector in a coprecipitate flotation (coflotation) method. Coflotation involves the coprecipitation of the ion to be removed with a suitable agent. The collector (usually a surfactant of a charge opposite to that of the coprecipitate) is then added to the suspension and well stirred whereby the collector is adsorbed onto the surfaces of the coprecipitate particles rendering them hydrophobic. The particles are then floated on the top of the surface of the bulk solution by introducing a gentle stream of fine gas bubbles. In treatment of medium active effluents, copper ferrocyanide has been found (22) to produce DF's in excess of 100 for Cs over pH 2-8. The same study recommends antimonic acid for strontium removal.

(viii) A new class of solid supports which may be considered as organic-inorganic ion exchangers of general formula $Zr(R\text{-}PO_3)_2$ and $Zr(R\text{-}OPO_3)_2$ have been synthesized (23). They may be considered as organic derivatives of α-ZrP in which the ≡P-OH tetrahedral groups are replaced by ≡P-R or ≡P-OR groups, where R represents an alkyl group. One organic-inorganic exchanger containing carboxyl groups, Zirconium bis(carboxymethanphosphonate), $Zr(HOOCCH_2PO_3)_2$, has recently been synthesized (24) and found to have surface ion exchange properties towards Mg^{2}, Ca^{2+}, Ba^{2+}, and La^{3+}.

It is very probable that with a suitable choice of different phosphoric acids (or esters) and also by replacing the zirconium with other tetravalent metals, several other inorganic-organic ion exchangers containing inorganic groups such as $-SO_3H$, $N-(CH_3)_3OH$ can similarly be prepared.

(ix) Synthesis of a composite ion exchanger composed of titanium hexacyanoferrate implanted into spherical beads of a phenol-sulphonic-formaldehyde resin has been described (25). High decontamination factors and stability over the pH interval 1-8 are mentioned. However, leakage of impurities such as sulphate and hexacyanoferrate ions in the ppm range has been noted.

In a very recent study (26) on the separation of caesium from nitric acid solutions of intermediate level waste from reprocessing of spent fuel elements (PUREX PROCESS), ammonium molybdophosphate has been found to show

excellent performance with high salt loadings and in a broad pH range from pH 9 to conc. HNO_3 with a capacity of 60g Cs/kg. Other inorganic exchange materials have shown high sorption values only for certain pH ranges:

- ammonium hexacyano cobaltous ferrate (pH12, 35g Cs/kg)
- potassium hexacyano nickel ferrate (pH10, 30g CS/kg)
- zirconium phosphate (pH 7, 100g Cs/kg)
- titanium phosphate (pH 7, 15g Cs/kg)
- antimony pentoxide (pH 2, 30g Cs/kg)
- titanium oxide (pH 7, 1g Cs/kg)

4.4 Macrocyclic Ligands. Crown compounds are known to have the ability to form stable and soluble organic complexes with the alkali and alkaline earth metals and have been investigated for removing Cs^+ and Sr^{2+} from acidic high acitivity nuclear waste (27).

Crown ethers and cryptands have been attached to organic polymer chains for use as ion exchange resins (28). It has also been shown that the presence of crown ethers in methanol-water solution markedly changes the distribution coefficients of alkali metal ions on commercial cation-exchange resins (29).

It has been known for a long time that ammonium phosphomolybdate (APM) acts as a highly selective ion exchanger towards alkali metals. Precipitate formation between crown ethers and phosphomolybdic acid gives a new class of ion exchangers which have a marked selectivity for the alkali metal ions (30). The ion binding in these precipitates is largely determined by the structure of the macrocyclic ether. The importance of the surface properties of the solid particles are reflected in the lack of reproducibility of results. So far there have been only a limited number of studies involving a limited number of crown ethers (eg, dicyclohexyl 18-Crown-6, dibenzo-18-Crown 6, 15-Crown-5, benzo-15-Crown-5 and dibenzo 24-Crown-8). Crown ethers specific for Cs such as benzo-12-crown-4 and other macrocyclic ligands have yet to be investigated.

The extractibility of a metal ion-crown ether pair into an organic solvent is strongly influenced by the lipophilic nature of the counteranion. A counteranion with a large molar volume, such as picrate, dinitrophenolate, dipicrylamine, and tetraphenylborate, tends to make the extraction of a metal ion-crown ether pair more effective. An alternative approach is to eliminate the need to extract an aqueous-phase anion by use of a macrocylic host to which is attached an appropriate negatively charged functional group. With crown ethers bearing

carboxylic acids as functional groups, it has been shown that the extraction of these metal ions by crown ether carboxylic acids is independent of counteranions. In an investigation (31) using Syn-dibenzo-16-crown-15-oxyacetic acid, high efficiencies have been observed in addition to significant selectivities in lanthanide extraction.

The first member of a new class of rigid, doughnut-shaped macrocycles that appear to have useful metal-binding properties has just been synthesized (32). The macrocycles are fully unsaturated analogs of 18-crown-6 ethers that have been made soluble by appropriate ligand substitution. They are believed to exhibit "useful kinetic and thermodynamic properties".

Recently some novel compounds known as, calixarenes which are water soluble have been synthesized and are of potential interest for heavy metals such as cobalt (33). The special feature of holding the four carboxylic acid groups on the same side of the molecule makes this compound attractive as a new complexone with a lipophilic backbone for the extraction and separation of metal ions.

4.5 Polymeric pseudocrown ethers. Many of these have been immobilized on organic polymers and used for complexation of transition metal anions (34). They are to be distinguished from polymers with pendant crown ethers attached to the network.

4.6 Immobilization of other functional groups specific for metal ions. Several studies have been reported on the incorporation of chelating functional groups. For instance, incorporation of an aminophenol type functional group has produced (35) a weak-base anion-exchange resin that removes ferric ions selectively in the presence of a wide range of uni- and multivalent metal ions and sulphate species.

Trace metal ion preconcentration for flame atomic absorption by an immobilized N,N,N^1-tri-(2-pyridylmethyl) ethylenediamine (TrPEN) chelate ion exchanger is reported (36) for a flow injection system.

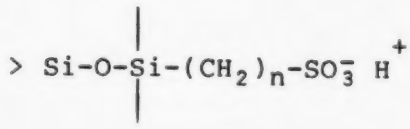
A chelating resin with a high capacity (3.16 meq of Pd^{2+}/g at pH 3.0) has been prepared from 5-chloromethyl-8-mercaptoquinoline and styrene-divinylbenzene copolymers (37).

Some studies have shown impregnation of organic resins (eg. Amberlite IRA 402) with citrates, EDTA, CyDTA or 1-nitroso-2-naphthol-3, 6-disulphonate produce sufficient selectivity towards copper and iron versus the rest of first row

transition metals, ie. short-lived nuclides may be separated from long-lived ones. These resins that selectively collect the short-lived nuclides could be usefully installed at suitable points upstream of the various ion exchangers, thus allowing the long-lived nuclides to be collected on the regular ion exchangers resulting in extended life. For the isolation and removal of short-lived nuclides, the best results have been obtained with Amberlite IRA-402 of 40-100 mesh, impregnated with citrate.

4.7 Biologically Active Systems. The use of immobilized microbes in the removal of specific pollutants from water and wastewater has recently been explored. The removal may be due to biodegradation and/or sorption to microbial cells. Removal of pesticides in water by microbial cells absorbed to magnetite is one of the few applications reported in the literature (38). Compared with physical and chemical processes for water purification, this area has so far received little attention and it may be rewarding to explore the possibilities on a long-term basis.

4.8 Glass-based ion exchangers. Porous glass-based ion exchangers have been suggested (39) as an alternative to conventional organic ion exchange resins. They may contain functional groups of conventional types (eg. sulphonic acid or quaternary amine groups) and other coordinating organic groups. The bonding is obtained by means of a silane reagent reacting with silica surface.



> Si- represents a silicon atom in a silica matrix.

They are a very strong alternative to conventional resins due to the following advantages:

(a) They should have a better radiation resistance.

(b) They could constitute their own waste matrix after a sintering operation which can take place at about 800-1000°C.

(c) Since = Si-O-Si-C bonds are stable up to about 350°C, they offer higher thermal resistance and hence it may not be necessary to pre-cool the PHT water before ion exchange.

(d) They produce much lower pressure drops for the same particle size and also lower swelling of the ion exchange material. They also have comparable or better kinetics of exchange and higher resistance to oil fouling.

(e) They have a better radiation resistance than conventional resins and gas evolution during long-term storage can be much reduced. They would be especially attractive in clean-up of highly radioactive waste solutions such as that would result in case of severe fuel damage releasing extraordinarily high radiation.

Their disadvantages and possible remedies will be discussed below:

(i) Their ion exchange capacities are generally lower than those of conventional resins and do not, normally exceed 2-2.5 meq/g. Their selectivities are however comparable. The effect from low ion exchange capacities will, possibly, be more than offset by greater volume reduction on sintering for final storage.

(ii) They have less resistance to low and high pH values. This can, probably, largely be circumvented by coating the porous silica material with an inert coating such as zirconia or titania before silanation.

(iii) They are more sensitive to mechanical wearing.

(iv) Although in dry systems = Si-O-Si-C bonds are stable up to about 350°C, = Si-C and = Si-N bonds tend to dissociate at about 250°C. In aqueous systems quantitative information on thermal stability is lacking.

A recent report (40) suggests applications in the treatment of both low-level and high-level radioactive streams in view of the high selectivity and effective capacity of the silica-based porous glass cation exchanger Durasil 10 for Cs, together with its high rate of ion exchange and its excellent chemical and mechanical stability.

The chelating qualities of 8-hydroxyquinoline (also known as 8-quinolinol or oxine) and its preference for transition, and heavy-metal cations relative to alkali and alkaline-earth cations are well known. These properties have led to a significant research effort in order to suitably immobilize this chelating agent onto various solid supports to utilize in ion exchange applications.

Amongst the various solid supports investigated, silica substrates (silica gel or glass beads) have been found to offer the advantages of good mechanical strength, resistance to swelling, and rapid overall exchange kinetics in column applications. However, they are unstable at high pH, leading to cleavage of the immobilized oxine and potential trace-metal contamination from the newly exposed silica surface.

4.9 Other Polymer Matrices. More recently (41), Fractogel-TSK, a highly porous, mechanically and chemically stable, hydrophillic organic resin gel has been investigated as a solid support for immobilization of oxine and it has been found to exhibit an exchange capacity comparable to the highest values reported for silica-immobilized 8-hydroxyquinoline and a greater stability at high pH.

Fractogel-TSK consists of intertwined vinyl polymer agglomerates, which offer mechanical and chemical stability, high porosity, and high hydrophilicity due to the presence of other linkages and hydroxyl groups. The hydroxyl groups (as secondary alcohols) enable relatively simple chemical modification for immobilization of oxine via phynol-azo linkages and also a wide range of other chelating groups. Further, the polymer itself exhibits no cation exchange capacity and does not concentrate dissolved organic species such as humic or fulvic acids.

Commercially available Courtelle fibres (polyacrylonitrile) have been chemically modified to contain imidazoline groups and the resultant cationic ion-exchange material is claimed (42) to possess an exchange capacity of 6.3 meq/g.

4.10 Proprietary Sorbents. Three lines of proprietary products have been identified for laboratory evaluations and arrangements are being made to obtain samples and pertinent information. Some specific products of interest are:

(a) Duratek glass-based ion exchange media with the sluiceable system concept. They are claimed to have greater effective capacity - typically 5-10 times greater than

organic resins. They are also claimed to have increased ion exchange kinetics (2-5 times faster than organics while yielding similar DF's). They are handled much the same as organic resins thus requiring little or no new hardware. The products to be tested will include:

(i) "Durasil 70": A carbon-based cation exchanger with a very high specificity for cobalt, and unaffected by high concentrations of sodium, potassium, calcium and magnesium.

(ii) "Durasil 10": A glass-based inorganic cation exchanger with a high specificity for the radioactive species caesium, cobalt, manganese and strontium, and low specificity for sodium and lithium.

(iii) "Durasil 230": Inorganic oxide based exchanger with proven high capacity for caesium removal at the North Anna radwaste water treatment plant.

(b) Devoe-Holbein Insoluble Chelating Compositions. Solid-state metal complexing materials derived from biological systems. The mechanism is based on that employed by living cells to capture required nutrient metals and to transport these throughout cells. In response to the depressed levels of free essential metals (eg. iron) in their immediate environment, most aerobic microbes synthesize and excrete into their surroundings low molecular weight, nonporphyrin, non-protein, metal-finding molecules collectively known as siderophores such as iron specific ligand molecules of the classes hydroxamates and phenolatecatecholates. They have very high complex formation constants viz for Fe (III) the range is 10^{30} to 10^{50}. Iron in natural siderophores is held tightly through coordination bonds to either the N- substituted hydroxomate moities of the desferrioxamine or the catechol moities of the Enterobactin. The same natural siderophores are known to bind some other metals but with a lower binding affinity.

Suitable modifications of synthetic catechol compositions, it is claimed by manufacturers, have produced sorbents with specific selectivities for (a) ^{137}Cs, ^{60}Co and ^{90}Sr in fuel bay water (b) ^{59}Fe and ^{60}Co in streams containing citrate complexes (c) ^{60}Co, ^{90}Sr, ^{137}Cs etc. from radwaste water and (d) ^{60}Co and

^{137}Cs from primary cooling water systems. These positive results have been demonstrated through field trials. Another useful aspect of these systems is their regenerability with 1-4 bed volumes of the regenerant solutions.

(c) Special Zeolites from Union Carbide. No further information is available as yet. Several special zeolites have been developed by Union Carbide and are said to be specific for caesium and cobalt.

5. PRELIMINARY EXPERIMENTS

During the present initial phase of the program, several commercially available sorbents chosen on the basis of manufacturers' claims and known general chemistry of the system are being tested in the laboratory for their selectivity towards cobalt - the species responsible for the major portion of the moderator liquid activity.

In order to identify suitable candidates for subsequent once-through and recirculation column tests, preliminary static batch tests have been conducted on several sorbents and their results are shown in Table 4. The solution used in these experiments contained copper, chromium, nickel, iron, zinc and manganese in addition to cobalt, in ratios very similar to those in actual moderator aqueous systems. Subsequent tests, however, were done using solutions containing cobalt as the only heavy metal. The results of these tests are given in Table 5.

6. DISCUSSION OF PRELIMINARY RESULTS

The results in Table 4 indicate the expected increase in adsorption capacity with increase in pH in both Duolite ES 467-Na^+ and IRC 718-Na^+ forms. These functional groups have a much higher affinity for protons than for metal ions. The ammonium form of the resin IRC 718 was tested to determine the effect of the counter ion and in this case shows a lower capacity at higher pH and this may be due to the lower stability of the NH_4^+ group. By far the highest capacity was observed for the resin currently in use-IRN 77-H^+. A-51 Na^+ and X-61 Na^+ together with ES 467 and IRC 718 are worthy of further investigation. These sorbents show comparable capacities for cobalt in the absence of other metal species as well, as can be seen in Table 5.

Table 6 shows the results of a study involving synergistic agents. This was based on the results of Ensor et al (43) who achieved differentiation in extraction of lanthanides in the

presence of crown ethers. A synergistic agent is a substance that in combination with another extractant causes the distribution of the metal ion to be greater than the sum of the distribution of the individual compounds. The size selective crown ethers in this particular study seem to have no significant effect on adsorption capacities of the various sorbents tested. The lack of effect with X-61 suggests that crown ethers are very poor coordinators as well.

It is interesting to note from Table 7 that the addition of cyclic ethers, in fact, produces a negative effect on the adsorption capacity of activated charcoal. This is presumably due to saturation of active sites on charcoal by the organic moities.

7. FUTURE WORK

7.1 In the second phase of the programme, comparative screening tests will be completed on some selected commercially available and nonproprietary sorbents. In all work, the currently used organic ion exchangers will be used as the bench mark for comparison. The work to date has been almost completely confined to the sorbents for cobalt removal from the moderator system. However, selective sorbents for other species/systems will also be examined.

7.2 Proprietary Sorbents: They will be tested as received. Initial static (batch) testing will be performed to select suitable candidates for column and subsequent testing.

7.3 Inorganic Ion Exchangers: Among these, attention will be confined mainly to the synthesis and/or testing of the following:

(a) Mordenites: These are some ion exchangeable porous zeolites granules with good selectivity for caesium.

(b) Chromium ferricyanide gel and the corresponding cobalt ferrocyanide gel both of which can be easily prepared and have already been tested by others.

(c) Hydrous zirconium oxide and zirconium phosphate. They show most promise for high temperature water purification.

(d) Lithium niobate crystals. They may show promise for cobalt and iron removal.

(e) Ammonium phosphomolybdate. In view of the recent claims, it is worthwhile studying the precipitate formation between crown ether and phosphomolybdic acid (30).

(f) Titanium antimonite for caesium removal. In this connection another alternative that will be considered is to identify and examine compositions showing high affinity for alkali and alkaline earth metals and show little or no affinity for transition and heavy metals which may be removed on the conventional ion exchange systems.

7.4 Porous Glass Exchangers: The proposed work on glass-based ion exchangers will include the following:

Synthesis of porous-glass exchangers containing various functional groups by reacting with various organosilanes:

(i) Phenol derivatives with substituent groups for potential caesium selectivity.

(ii) Incorporation of caesium specific macrocylic ligands such as crown ethers, using suitable reagents (27).

eg. Bis (4,4'(5')-[1-hydroxyheptyl]benzo-18-Crown-6.

The specificity has been attributed to steric hindrance effects.

(iii) Incorporation of chelating ligands of potential affinity towards cobalt and iron etc.

eg. "ONNN" group as chelating and preconcentrating substances of heavy metal ions (44).

N,N,N^1-tri(2-pyridylmethyl) ethylene diamine (Tri PEN)

A successful procedure for its synthesis already exists (45).

7.5 Synthesis of organic ion exchange resins with novel chelating groups: The above functional groups and any others that might be realized as the work progresses will be considered for incorporation.

It will be first attempted to convert existing commercially available resins by simple reaction routes to suitable chelating resins.

The other types of chelating groups of interest would be the ones found in natural biological systems as discussed earlier. Attempts will be made to synthesize chelating groups modelled onthese biological systems of high specificity.

7.6 Synthesis of Fractogel-TSK with Chelating Functional Groups: Attempts will be made to immobilize oxine and other related functional groups with high selectivity and capacity for metals of interest.

In general, all studies will involve static tests to determine the capacity and selectivity of various sorbents using simulated process compositions, followed by dynamic (column) testing for operating capacities. Column experiments will also be used to study process engineering parameters such as effects of temperature, pH, mechanical wearing and impurity release etc. Reactor applications will be studied on-line at a reactor site using small test columns (~100 mL) in a loop of an existing circuit.

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TABLE 1

Ion Exchange Resin Usage in Major Purification Systems

Purification System	Resin Designation	Resin Description	Annual Usage (cubic metre)
PHT	Amberlite IRN-154 LC	Li^+/OH^- Mixed Bed	25
Moderator	Amberlite IRN-150 LC	H^+/OH^- Mixed Bed	75
Moderator	Ionac M-757	H^+/FB^- Mixed Bed	10
IFB	Amberlite IRN-150 LC	H^+/OH^- Mixed Bed	10

IRN - 154 LC ⟶ IRN 163 in Li^+ form (parent resin IR-120)
⟶ IRN 78 in OH^- form

IRN - 150 LC ⟶ IRN 77, 1.8 meq/mL, in H^+ form (parent resin IR-120)
IRN 78 in OH^- form

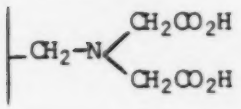
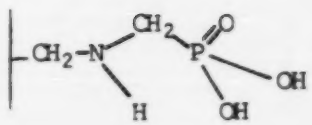
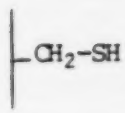
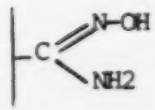
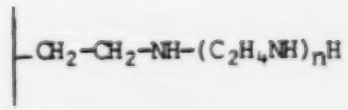
TABLE 2

Chemistry Control Parameters

Parameter	System		
	PHT	Moderator	IFB
pH (25°C)	10.3-10.7	4.5-7.0	5.8-9.0
Conductivity mS/m (25°C)	2.2-3.5	<0.3	<0.2
Chloride (mgCl/kg)	<0.1	<0.1	<0.3
Boron (mgB/kg	-	<10	-
Gd (mgG/kg)	-	<1 (Xe substitution or 10-20 (following SDS2)	-
Li (mg Li/kg)	0.8-1.3		-
^{131}I (μCi/kg)			<20

TABLE 3

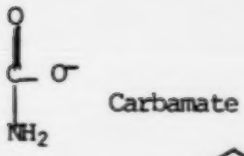
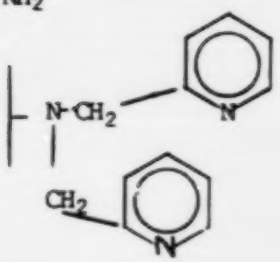
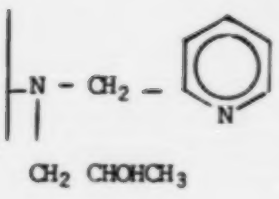
Chelating Resins

RESIN	FUNCTIONAL GR.	SUPPLIER	COMMENTS
Diaion CR-10® Amberlite IRC-718 or Dowex A-1® Wofatit MC-50®		R&H/Dow	
Duolite SE 467		R&H/DS	Properties intermediate between strong and weak acids
Ionac SR-3 Srafion NMRR®	Polyisothiouronium	Ionac/Sybrion Ayalon (Israel)	
IMAC-TMR®		AKZO Chemical Co (Netherlands)	Used for removal of Hg from waste water
Duolite ES-346 Diaion CR50		DS/Mitsubishi	
Polyethyleneamine Diaion CR-20®		Mitsubishi	

(Continued Over)

TABLE 3 (Cont'd)

Chelating Resins

RESIN	FUNCTIONAL GR.	SUPPLIER	COMMENTS
Nisso Alm®	 Carbamate	Nippon Soda.	
XFS-4195		Dow Chemicals	Good for Co^{2+}
XFS-43084		Dow Chemicals	Co^{2+}

SPECIAL RESINS

RESIN	FUNCTIONAL GR.	SUPPLIER	COMMENTS
Duolite GT-73	Weakly acidic functional gr. -COOH .	R&H	Good for Co^{2+} pH 1-13 originally from Akzo Zout chemie The Netherlands

TABLE 4

Results of Tests Done with Multication Solutions

Sorbent	pH	Adsorption Capacity (mg Co/g adsorbent)	Comments
Duolite ES 467-Na^+	4.7	1.20	Amino Phosphonic Gr.
	6.3	1.53	
IRC 718 - Na^+	4.7	1.20	Iminodiacetic Acid
	6.3	1.85	
- NH_4^+	4.7	1.06	" "
	6.3	0.61	
IR 120 - H^+ or IRN 77 - H^+	4.7	1.21	Strong Cation Resin Used in Mod. System
	6.3	2.16	
GT 73 - H^+	4.7	0.35	Weakly Acidic Cation Resin
	6.3	0.15	
Dow XFS 4195	4.7	0.33	BIS Picolylamine Functional Gr.
	6.3	0.34	
Dow XFS 43084	4.7	0.08	Mono Picolyl - 2-Hydroxy Propylamine
	6.3	0.01	
K-MAC	4.7	0.30	Activated Charcoal Impregnated With Oxine
	6.3	0.24	
A-51 Na^+	6.5	1.46	Inorganic IX Based on Alkali Metal Alumino-Silicate
X-61 Na^+	6.5	1.53	" "

TABLE 5

Cobalt Capacities in the Absence of Other Heavy Metals

Sorbent	pH	Adsorption Capacity (mg Co/g adsorbent)	Comments
ES 467 - Na^+	5.4	37.7	
	7.0	39.0	
IRC 718 - Na^+	5.4	39.0	
	7.0	36.6	
IR 120 - H^+ or IRN 77 - H^+	5.4	40.3	
	7.0	>40.6	
A-51 - Na^+	5.4	39.2	
X-61 - Na^+	5.4	37.1	
K-MAC(as received)	5.4	4.35	
	7.0	10.2	
K-MAC(freshly made)	7.0	7.9	
Diaion CR50	7.0	NIL	Amidoxime Functional Gr.
Diaion CR55X	7.0	NIL	Amidoxime Functional Gr.

TABLE 6

Effect of Synergistic Agents

Sample	Synergistic Agent/Concentration (m moles/L)		Cobalt Adsorption Capacity (mg/g of resin)
	Initial pH = 5.6 Initial Cobalt Concentration = 920 mg/L		
IRN 77-H^+	-	-	46.9
IRN 77-H^+	18-Crown-6	1.87	47.5
IRN 77-H^+	18-Crown-6	7.47	
IRN 77-H^+	15-Crown-5	1.87	47.4
IRC 718-Na^+	-	-	37.2
IRC 718-Na^+	18-Crown-6	1.87	37.2
IRC 718-Na^+	15-Crown-5	1.87	37.1
	pH = 5.6 Initial Cobalt Concentration = 1160 mg/L		
IRN 77-H^+	-	-	61.2
IRN 77-H^+	12-Crown-4	3.80	61.4
IRC 718-Na^+	-	-	46.7
IRC 718-Na^+	12-Crown-4	3.80	47.0
X-61	-	-	45.7
X-61	12-Crown-4	3.80	45.6
X-61	18-Crown-6	2.53	46.8

TABLE 7

Performance of Activated Charcoal Impregnated with Chelating Organic Groups

pH = 5.6
Cobalt Concentration = 1110 mg/L

Adsorbent	Concentration of Chelating Group	Adsorption Capacity for Cobalt (mg/g Sorbent)
Activated Charcoal	-	12.0
18-Crown-6 on Charcoal	4% (w/w)	1.8
Dibenzo-1-Crown-6 on Charcoal	8% (w/w)	6.4
8-Hydrozyquinoline on charcoal (K-MAC)	10% (w/w)	9.0

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